organic compounds

Methyl 3-cyclohexylidenedithio-carbazate

Yu-Liang Tian,[a] Shan-Heng Wang,[a] Shang Shan[a]* and Xu-Chun Fu[b]

[a]College of Chemical Engineering and Materials Science, Zhejiang University of Technology, People's Republic of China, and [b]Department of Pharmacy, Zhejiang University City College, People's Republic of China
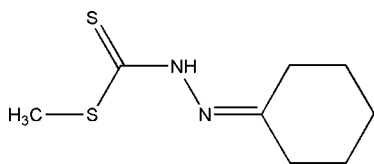Correspondence e-mail: shanshang@mail.hz.zj.cn

In the title compound, $C_8H_{14}N_2S_2$, the ring displays a normal chair conformation. An appreciable difference in C—S bond distances is observed within the dithiocarboxyl group. Intermolecular N—H···S and C—H···S hydrogen bonds link adjacent molecules, forming a centrosymmetric supramolecular dimer.

Related literature

For general background, see: Okabe *et al.* (1993); Hu *et al.* (2001); Shan *et al.* (2003). For a related structure, see: Chen *et al.* (2007). For synthesis, see: Hu *et al.* (2001).

Experimental

Crystal data

$C_8H_{14}N_2S_2$	$V = 1076.1$ (3) Å³
$M_r = 202.33$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 11.4552$ (12) Å	$\mu = 0.45$ mm⁻¹
$b = 8.2233$ (14) Å	$T = 294$ (2) K
$c = 11.5627$ (14) Å	$0.42 \times 0.30 \times 0.20$ mm
$\beta = 98.904$ (12)°	

Data collection

Rigaku R-AXIS RAPID IP diffractometer	10244 measured reflections
	2447 independent reflections
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	1517 reflections with $I > 2\sigma(I)$
$T_{min} = 0.775$, $T_{max} = 0.910$	$R_{int} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$	111 parameters
$wR(F^2) = 0.133$	H-atom parameters constrained
$S = 1.09$	$\Delta\rho_{max} = 0.31$ e Å⁻³
2447 reflections	$\Delta\rho_{min} = -0.28$ e Å⁻³

Table 1
Selected geometric parameters (Å, °).

S1—C7	1.657 (2)	S2—C8	1.796 (3)
S2—C7	1.749 (2)	N1—C1	1.281 (3)
N2—C7—S1	121.71 (17)	S1—C7—S2	125.26 (14)
N2—C7—S2	113.03 (17)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2N···S1[i]	0.90	2.71	3.592 (2)	164
C6—H6B···S1[i]	0.97	2.74	3.555 (3)	141

Symmetry code: (i) $-x, -y+1, -z+1$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
Chen, Z.-Y., Wu, G.-Q., Jiang, F.-X., Tian, Y.-L. & Shan, S. (2007). *Acta Cryst.* E**63**, o1919–o1920.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Hu, W., Sun, N. & Yang, Z. (2001). *Chem. J. Chin. Univ.* **22**, 2014–2017.
Okabe, N., Nakamura, T. & Fukuda, H. (1993). *Acta Cryst.* C**49**, 1678–1680.
Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2002). *CrystalStructure*. Version 3.00. Rigaku/MSC, The Woodlands, Texas, USA.
Shan, S., Xu, D.-J., Hung, C.-H., Wu, J.-Y. & Chiang, M. Y. (2003). *Acta Cryst.* C**59**, o135–o136.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

doi:10.1107/S1600536807056401

supplementary materials

Methyl 3-cyclohexylidenedithiocarbazate

Y.-L. Tian, S.-H. Wang, S. Shan and X.-C. Fu

Comment

Hydrazone and its derivatives have attracted our much attention because of their application in biological field (Okabe *et al.*, 1993; Hu *et al.*, 2001). As part of our ongoing investigation on anti-cancer compounds (Shan *et al.*, 2003), the title compound has been prepared and its structure is presented here.

The molecular structure of the title compound is shown in Fig. 1. The cyclohexylene ring displays a normal chair conformation. The N1═C1 bond distance of 1.281 (3) Å indicates a typical C═N double bond. The S1—C7 bod distance is appreciably shorter than S2—C7 bond distance. The N2—C7—S2 bond angle is significantly smaller than N2—C7—S1 bond angle (Table 1), which is similar to that found in a related compound methyl (β-*N*-thiazole-ethylene)dithiocarbazate (Chen *et al.*, 2007).

Inter-molecular N—H⋯S and C—H⋯S hydrogen bonding (Table 2) links adjacent molecules to form the centro-symmetric supra-molecular dimer (Fig. 2).

Experimental

Methyl dithiocarbazate was synthesized in the manner reported previously (Hu *et al.*, 2001). Methyl dithiocarbazate (1.24 g, 10 mmol) and cyclohexanone (0.98 g, 10 mmol) were dissolved in ethanol (10 ml) and the solution was refluxed for 4 h. After the solution cooled to room temperature, yellow fine crystals appeared. They were separated and washed with cold water three times. The single crystals were obtained by recrystallization form an absolute ethanol solution.

Refinement

Methyl H atoms were placed in calculated positions with C—H = 0.96 Å and torsion angle was refined to fit electron density, $U_{iso}(H) = 1.5U_{eq}(C)$. Other H atoms were placed in calculated positions with C—H = 0.97 and N—H = 0.86 Å, and refined in the riding mode with $U_{iso}(H) = 1.2U_{eq}(C,N)$.
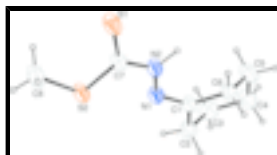
Figures

Fig. 1. The molecular structure of the title compound with 40% probability displacement ellipsoids (arbitrary spheres for H atoms).
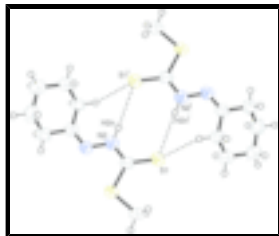
Fig. 2. A diagram showing hydrogen bonding [symmetry code: (i) −x,1 − y,1 − z].

Methyl 3-cyclohexylidenedithiocarbazate

Crystal data

$C_8H_{14}N_2S_2$	$F_{000} = 432$
$M_r = 202.33$	$D_x = 1.249$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 6268 reflections
$a = 11.4552$ (12) Å	$\theta = 3.5–26.0º$
$b = 8.2233$ (14) Å	$\mu = 0.45$ mm^{-1}
$c = 11.5627$ (14) Å	$T = 294$ (2) K
$\beta = 98.904$ (12)º	Prism, yellow
$V = 1076.1$ (3) Å^3	$0.42 \times 0.30 \times 0.20$ mm
$Z = 4$	

Data collection

Rigaku R-AXIS RAPID IP diffractometer	2447 independent reflections
Radiation source: fine-focus sealed tube	1517 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.034$
Detector resolution: 10.00 pixels mm^{-1}	$\theta_{max} = 27.4º$
$T = 294(2)$ K	$\theta_{min} = 3.1º$
ω scans	$h = -12 \rightarrow 14$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$k = -10 \rightarrow 10$
$T_{min} = 0.775$, $T_{max} = 0.910$	$l = -14 \rightarrow 14$
10244 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.035$	$w = 1/[\sigma^2(F_o^2) + (0.0604P)^2 + 0.2675P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.133$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.09$	$\Delta\rho_{max} = 0.31$ e Å^{-3}

2447 reflections

$\Delta\rho_{min} = -0.28$ e Å^{-3}

111 parameters

Extinction correction: SHELXL, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Primary atom site location: structure-invariant direct methods

Extinction coefficient: 0.013 (3)

Secondary atom site location: difference Fourier map

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of F^2 > 2sigma(F^2) is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
S1	0.10291 (6)	0.46402 (12)	0.35779 (6)	0.0773 (3)
S2	0.35920 (5)	0.42716 (9)	0.46671 (5)	0.0630 (2)
N1	0.27455 (16)	0.4020 (2)	0.67356 (16)	0.0540 (5)
N2	0.18167 (16)	0.4126 (2)	0.57986 (16)	0.0530 (5)
H2N	0.1054	0.4225	0.5906	0.064*
C1	0.25006 (19)	0.3598 (3)	0.77372 (19)	0.0513 (5)
C2	0.3507 (2)	0.3589 (4)	0.8739 (2)	0.0655 (7)
H2A	0.4219	0.3979	0.8471	0.079*
H2B	0.3650	0.2487	0.9024	0.079*
C3	0.3220 (3)	0.4675 (4)	0.9729 (2)	0.0760 (8)
H3A	0.3843	0.4577	1.0397	0.091*
H3B	0.3189	0.5800	0.9474	0.091*
C4	0.2051 (3)	0.4216 (4)	1.0095 (2)	0.0786 (8)
H4A	0.1872	0.4971	1.0688	0.094*
H4B	0.2111	0.3135	1.0435	0.094*
C5	0.1054 (3)	0.4246 (4)	0.9055 (2)	0.0753 (8)
H5A	0.0328	0.3883	0.9306	0.090*
H5B	0.0936	0.5352	0.8770	0.090*
C6	0.1333 (2)	0.3154 (3)	0.8067 (2)	0.0575 (6)
H6A	0.1348	0.2027	0.8317	0.069*
H6B	0.0721	0.3271	0.7392	0.069*
C7	0.20745 (19)	0.4343 (3)	0.4719 (2)	0.0516 (5)
C8	0.3644 (3)	0.4656 (5)	0.3147 (2)	0.0864 (10)
H8A	0.3264	0.3781	0.2684	0.130*
H8B	0.4453	0.4733	0.3026	0.130*
H8C	0.3244	0.5658	0.2919	0.130*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0434 (4)	0.1320 (7)	0.0561 (4)	0.0070 (4)	0.0068 (3)	0.0009 (4)
S2	0.0401 (3)	0.0964 (5)	0.0539 (4)	0.0071 (3)	0.0123 (2)	0.0004 (3)
N1	0.0425 (10)	0.0667 (12)	0.0537 (11)	−0.0026 (8)	0.0102 (8)	0.0005 (9)
N2	0.0403 (10)	0.0662 (12)	0.0544 (11)	−0.0018 (8)	0.0131 (8)	0.0007 (9)
C1	0.0465 (12)	0.0544 (13)	0.0546 (13)	0.0003 (10)	0.0133 (10)	0.0003 (11)
C2	0.0494 (14)	0.0860 (18)	0.0614 (14)	0.0003 (12)	0.0094 (11)	0.0114 (14)
C3	0.0787 (19)	0.0818 (19)	0.0631 (16)	−0.0097 (15)	−0.0028 (14)	−0.0004 (14)
C4	0.079 (2)	0.102 (2)	0.0569 (15)	0.0075 (16)	0.0163 (14)	−0.0085 (15)
C5	0.0629 (17)	0.100 (2)	0.0666 (16)	0.0120 (15)	0.0202 (13)	−0.0051 (15)
C6	0.0487 (13)	0.0668 (15)	0.0587 (13)	−0.0017 (11)	0.0142 (10)	0.0065 (12)
C7	0.0421 (12)	0.0588 (13)	0.0559 (13)	0.0004 (10)	0.0140 (10)	−0.0048 (10)
C8	0.0574 (17)	0.148 (3)	0.0572 (16)	0.0104 (17)	0.0213 (13)	0.0033 (17)

Geometric parameters (Å, °)

S1—C7	1.657 (2)	C3—H3A	0.9700
S2—C7	1.749 (2)	C3—H3B	0.9700
S2—C8	1.796 (3)	C4—C5	1.525 (4)
N1—C1	1.281 (3)	C4—H4A	0.9700
N1—N2	1.399 (3)	C4—H4B	0.9700
N2—C7	1.339 (3)	C5—C6	1.526 (4)
N2—H2N	0.9052	C5—H5A	0.9700
C1—C6	1.491 (3)	C5—H5B	0.9700
C1—C2	1.502 (3)	C6—H6A	0.9700
C2—C3	1.528 (4)	C6—H6B	0.9700
C2—H2A	0.9700	C8—H8A	0.9600
C2—H2B	0.9700	C8—H8B	0.9600
C3—C4	1.512 (4)	C8—H8C	0.9600
C7—S2—C8	102.20 (13)	C5—C4—H4B	109.4
C1—N1—N2	118.06 (19)	H4A—C4—H4B	108.0
C7—N2—N1	118.65 (18)	C6—C5—C4	111.3 (2)
C7—N2—H2N	118.3	C6—C5—H5A	109.4
N1—N2—H2N	122.3	C4—C5—H5A	109.4
N1—C1—C6	128.9 (2)	C6—C5—H5B	109.4
N1—C1—C2	116.7 (2)	C4—C5—H5B	109.4
C6—C1—C2	114.43 (19)	H5A—C5—H5B	108.0
C1—C2—C3	110.3 (2)	C1—C6—C5	110.3 (2)
C1—C2—H2A	109.6	C1—C6—H6A	109.6
C3—C2—H2A	109.6	C5—C6—H6A	109.6
C1—C2—H2B	109.6	C1—C6—H6B	109.6
C3—C2—H2B	109.6	C5—C6—H6B	109.6
H2A—C2—H2B	108.1	H6A—C6—H6B	108.1
C4—C3—C2	111.5 (2)	N2—C7—S1	121.71 (17)
C4—C3—H3A	109.3	N2—C7—S2	113.03 (17)

C2—C3—H3A	109.3	S1—C7—S2	125.26 (14)
C4—C3—H3B	109.3	S2—C8—H8A	109.5
C2—C3—H3B	109.3	S2—C8—H8B	109.5
H3A—C3—H3B	108.0	H8A—C8—H8B	109.5
C3—C4—C5	111.3 (2)	S2—C8—H8C	109.5
C3—C4—H4A	109.4	H8A—C8—H8C	109.5
C5—C4—H4A	109.4	H8B—C8—H8C	109.5
C3—C4—H4B	109.4		

Hydrogen-bond geometry (Å, °)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N2—H2N⋯S1[i]	0.90	2.71	3.592 (2)	164
C6—H6B⋯S1[i]	0.97	2.74	3.555 (3)	141

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1.

Fig. 1

Fig. 2